

Overview of Chapter 8

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8.0 Introduction**8.1 Background**

Petroleum fuel and oil products represent the single most common environmental contaminant in Indiana. Common sources of these products are motor fuel station underground storage tanks, home and commercial heating oil storage tanks, fuel distribution centers, refineries, crude oil production sites, and accidental spills. In Indiana, alone, there are over 19,000 registered underground storage tanks and over 7,000 confirmed leaks have been reported. These leaks can range from a few gallons to many thousands of gallons.

Petroleum fuels and oils are complex mixtures of hydrocarbons that vary, not only among the fuel types, but also within each fuel type depending upon manufacturer, geographic location, and seasonal use. The compositions of these products are made up of several hundred hydrocarbon compounds. Of these hundreds of compounds, toxicological information is available on only a very few. This makes determining the health risk posed by petroleum hydrocarbons difficult.

Traditionally, petroleum fuel or oil contaminated sites have been characterized by two measures; specific indicator compounds called the chemicals of concern (COCs) and by the total of all the petroleum hydrocarbons, called total petroleum hydrocarbons (TPH). The individual COCs had human health risk derived closure levels, but TPH did not have closure levels based upon human health effects. The Total Petroleum Hydrocarbons Criteria Work Group (TPHCWG) and the states of Washington and Massachusetts have developed approaches that enable the development of human health risk-based closure levels for TPH. IDEM fundamentally agrees with these approaches and has developed similar procedures. The TPH closure levels are based on the non-cancer end points of exposure. IDEM addresses the carcinogenic exposure by analysis for certain carcinogenic COCs (benzene and certain carcinogenic polycyclic aromatic hydrocarbons, cPAHs). Additionally, IDEM still requires source area measurement of certain non-carcinogenic COCs (n-hexane, naphthalene, toluene, ethylbenzene, and xylene, plus non-carcinogenic PAHs for waste oil). The COCs for petroleum products are listed in Appendix 4.1, RISC User's Guide.

This new approach breaks down the composition of specific petroleum products into chemical groups, called fractions, based upon carbon chain length and similar physical/chemical properties. Because the composition of each fraction is variable, and toxicological information

is not available for every compound in each fraction, the physical/chemical and toxicological properties of one or more surrogate compounds are chosen to represent each fraction. A TPH closure level for each major hydrocarbon product type in soil and ground water can then be determined based upon the sum of the individual fractions.

8.1.2 Purpose and Scope

The purpose of this chapter is to:

- Provide human health risk-based closure levels for source areas on sites contaminated with TPH.
- Provide details on this new approach.
- Provide details on site evaluation techniques that are unique to TPH.

This chapter is focused on how the health-based closure levels for TPH were determined and how those closure levels are applied at petroleum contaminated sites. Specific guidance on the COCs is found in the RISC Technical Guide and the RISC User's Guide, (Chapter 3 and Appendix 4.1, 4.2).

8.1.3 Applicability

The provisions of this chapter apply to all sites that are contaminated by releases of petroleum hydrocarbon products and/or lubricating oils and are addressed by the Leaking Underground Storage Tank Program (LUST), Voluntary Remediation Program (VRP), State Cleanup Program, Brownfields Program, and RCRA Corrective Action Program. In general, IDEM will not require reevaluation of petroleum hydrocarbon contaminated sites that were closed properly prior to the effective date of this NPD. However, the Agency reserves the right, under IC 13-14-2-1; IC 13-23-13; IC 13-24-1; and IC 13-25-5-17, to reevaluate sites where compelling evidence indicates that significant human health or ecological risks exist. Examples of such situations may be when hydrocarbon products have impacted drinking water wells above default closure levels for TPH or COCs, or where hydrocarbon vapors have intruded into indoor air spaces.

The provisions of this chapter do not apply to hydrocarbon releases at manufactured gas plants (MGPs).

8.1.4 Effective Date

The provisions of this chapter will be effective 30 days after the presentation to the Solid Waste Management Board.

8.1.4.1 Implementation Milestones

- **Leaking Underground Storage Tank program** - All LUST site responsible parties who file an Initial Incident Report on or after the effective date of this NPD should follow this guidance for TPH as well as COC closure levels. Responsible parties who filed an Initial Incident Report prior to the effective date of this NPD may continue to evaluate and close their sites under the preexisting guidance and closure levels or, with IDEM's written approval, choose to use this guidance.
- **Voluntary Remediation Program** – All VRP site responsible parties that have a Voluntary Remediation Agreement (VRA) approved and signed by IDEM on or after the effective date of this NPD should follow this guidance. VRAs approved and signed prior to the effective date of this NPD may continue to evaluate and close their sites under the preexisting guidance and closure levels or, with IDEM's written approval, choose to use this guidance.
- **State Cleanup Program** – All State Cleanup program responsible parties that have an Agreed Order signed on or after the effective date of this NPD should follow this guidance. Agreed Orders signed prior to the effective date of this NPD may continue to evaluate and close their sites under the preexisting guidance and closure levels or, with IDEM's written approval, choose to use this guidance.
- **Brownfields Program** – All Brownfield Program evaluations of TPH should follow this guidance after the effective date of this NPD.
- **RCRA Corrective Action** – All RCRA Corrective Action site responsible parties that submit a Facility Investigation Work Plan on or after the effective date of this NPD should follow this guidance. Facility Investigation Work Plans submitted prior to the effective date of this NPD may continue to evaluate and close their sites under the preexisting guidance and closure levels or, with IDEM's written approval, choose to use this guidance.

8.2 Summary of Approach

8.2.1 Concept

For the purposes of this guidance, the term TPH refers to petroleum hydrocarbon mixtures composed of compounds with carbon numbers ranging from C₅ through C₃₆ that originated from petroleum and have been analyzed by EPA Modified Method 8015D.

Petroleum hydrocarbon products are mixtures of over 250 hydrocarbon compounds. The various product mixtures produced by the manufacturers are based upon physical and performance-based criteria and not specific formulas. As a result, the product compositions can vary depending upon, in part, the crude oil refined to produce the product, the type of product, the season of the year, and any performance additives.

Petroleum hydrocarbon products are also subject to changes in composition once they are released into the environment. The lower molecular weight hydrocarbons are generally more volatile and water-soluble than are the higher molecular weight hydrocarbons. Some of the lower molecular weight hydrocarbons are also more subject to microbial decomposition and the degradation products might include compounds not originally found in the product.

It is not practical to identify and quantify all of the individual compounds contained in a particular hydrocarbon fuel or oil. A further difficulty is that the necessary toxicological information is available for only about 25 of these compounds. The fractionation approach addresses these complications by dividing the hydrocarbon mixture into several fractions that are sufficiently homogeneous with respect to physical and chemical properties. A surrogate compound, (or a mixture with characteristics similar to the fraction), on which adequate toxicological information exists, is selected to represent each fraction. That surrogate is then used to estimate the potential human health risks posed by that fraction. The individual risks of each fraction are then totaled to evaluate the overall risk of the hydrocarbon product.

8.2.2 TPH Fractions

For analysis, TPH is broken down into 12 fractions having similar physical-chemical properties within each fraction. These 12 fractions are composed of seven aliphatic (a broad category of carbon compounds distinguished by a straight, or branched, open chain arrangement of the constituent carbon atoms) and five aromatic (benzene ring compounds) fractions. Each fraction is defined by a range of equivalent carbon (EC) numbers. The EC number is related to

a compound's boiling point and retention time on a gas chromatography (GC) column normalized to the actual carbon numbers of n-alkanes. For example, the EC of benzene, a cyclic 6-carbon aromatic compound, is 6.5 because its boiling point and GC retention time are halfway between those of n-hexane (a straight 6-carbon chain compound) and n-heptane (a straight 7-carbon chain compound). The EC numbers are used because they are more closely related to environmental mobility. Surrogate compounds are then selected to represent the toxicological properties of each fraction. While the toxicities of some fractions may be represented by the same surrogate compound, the physical and chemical properties are specific for each fraction. Thus, each fraction is unique. The hydrocarbon fractions, surrogates, toxicological information, and analytical methods are given in Table 2-1. It should be noted that the aromatic fractions EC>5-7 and EC>7-8 are not included because these fractions are almost entirely made up of benzene, ethylbenzene, toluene, and xylene and they are evaluated as COCs.

8.2.3 Toxicology

Based upon the available information on the chemistry and toxicology of petroleum hydrocarbons, it is possible to make the following generalizations:

- Petroleum hydrocarbon fuels and oils are mainly composed of aliphatic and aromatic hydrocarbon compounds.
- Petroleum aromatic hydrocarbons generally appear to be more toxic than petroleum aliphatic compounds.

8.2.3.1 Non-Cancer Toxicity

The non-cancer toxicity of TPH is based upon the non-cancer toxicity of specific hydrocarbons selected to represent specific groups of hydrocarbons (fractions) that compose typical products. A toxicity value (oral and inhalation Reference Doses) for each fraction is based upon a representative compound for that fraction. The hazard quotient (HQ) for each fraction is calculated and then summed to determine the hazard index (HI) for the product. The HI is then used to determine the closure level that would be equivalent to a HI = 1. Table 2-1 contains the Non-Cancer reference doses.

8.2.3.2 Cancer Toxicity

The cancer effects of the products are evaluated by quantifying specific chemical compounds that are designated as carcinogens, such as benzene, and certain carcinogenic polycyclic aromatic hydrocarbons

(cPAHs). For waste oil, additional PAH compounds are also quantified (See *Waste Oil Analyses and Analytes*, at http://www.in.gov/idem/programs/land/lust/waste_oil.html) The cancer risk must be less than, or equal to, 1×10^{-5} (one in one hundred thousand). For additional information on determining cancer effects see the RISC Technical Guide, Appendix 1. See Appendix 4.1 of the RISC User's Guide for the chemicals of concern for various petroleum products.

Table 2-1 Hydrocarbon Fractions, Their Reference Doses, and Analytical Methods

HYDROCARBON FRACTIONS				
Hydrocarbon Fractions	Surrogate	Reference Dose mg/kg - day		Analytical Method***
Aliphatic		Oral	Inhalation	
EC 5-6	Cyclohexane	1.7	1.7	VPH
EC > 6-8	Cyclohexane	1.7	1.7	VPH
EC > 8-10	JP – 8*	0.03	0.085	VPH/EPH
EC > 10-12	JP – 8*	0.03	0.085	VPH/EPH
EC > 12-16	JP – 8*	0.03	0.085	EPH
EC > 16-21	White Mineral Oil	2.0	NA	EPH
EC > 21-36	White Mineral Oil	2.0	NA	EPH
Aromatic				
EC 8-10	Naphthalene	0.02	0.02**	VPH
EC > 10-12	Naphthalene	0.02	0.02**	VPH/EPH
EC > 12-16	Naphthalene	0.02	0.02**	EPH
EC > 16-21	Pyrene	0.03	NA	EPH
EC > 21-36	Pyrene	0.03	NA	EPH

* Jet fuel

** Route extrapolated

*** See <http://www.ecy.wa.gov/biblio/97602.html> for the analytical methods for volatile petroleum hydrocarbons (VPH) and extractable petroleum hydrocarbons (EPH).

8.3 Closure Levels

RISC has developed a default/non-default approach to determining the TPH closure levels at sites (Table 3-1). Default TPH closure levels have been determined for gasoline range organics and diesel range organics from fractionation analysis of theoretical formulations of gasoline and diesel fuel. The closure levels for diesel range organics apply to all of the mid-range liquid hydrocarbon products, high end hydrocarbon oils, and waste motor oil.

8.3.1 Default Closure Levels

Consistent with RISC, the default soil closure levels are the more health protective of the surface soil or subsurface soil closure levels. The default soil and ground water TPH closure levels are based upon fraction analysis of a theoretical gasoline composition and a theoretical diesel fuel composition. Limited experience with fractionation of diesel contaminated soils have yielded some site specific closure levels lower than the default closure levels that were based upon a theoretical diesel composition. Because of this, a margin of safety has been added to the diesel fuel default closure level to address this concern. As data are accumulated on products in Indiana, the default compositions (and the resultant default closure levels) may be adjusted to more closely reflect the actual petroleum products. Gasoline and diesel COC closure levels must be met in both the soil and ground water.

When the petroleum contamination is a mixture of gasoline and diesel fuel, the default closure level of the mixture can be determined by the sum of the ratio of the gasoline (GRO) concentration to the default gasoline closure level and the ratio of the diesel (ERO) concentration to the default diesel closure level being equal to a hazard index of 1, as follows:

$$1 = [\text{GRO}]/330 + [\text{ERO}]/1,000$$

8.3.2 Non-default Closure Levels

Non-default closure levels provide for site-specific closure levels using the Washington Department of Ecology's 12 fraction VPH/EPH analyses. The method of deriving the closure levels (default and non-default) is described in detail in Appendix 8. Non-default TPH closure levels are site-specific and are based upon fraction analysis of site-specific product compositions. TPH is regulated as the sum of the

fractions and not by the individual fractions. The individual fractions do not have closure levels assigned to them.

Table 3-1 TPH Closure Levels

TPH Closure Levels[†]						
	Hydrocarbon Product	Soil (mg/kg)		Ground Water (µg/l)		Caveat
		Commercial/Industrial	Residential	Commercial/Industrial	Residential	
Default	Gasoline	330	25	3,000	220	No Free Product
	Diesel	1,000	80	1,100	100	No Free Product
Non-default	Gasoline	Site Specific (< 2,000)	Site Specific (< 1,000)	Site Specific	Site Specific	No Free Product
	Diesel	Site Specific (< 10,000)	Site Specific (< 5,000)	Site Specific	Site Specific	No Free Product
†See the RISC User's Guide, Appendix 4, for the COCs. COCs are determined in soil and ground water.						

8.3.3 Maximum TPH Contaminant Concentrations

Because high concentrations (>1%) of petroleum hydrocarbons in soil have demonstrated phytotoxic properties, as well as the uncertainty about the fate and transport of high concentrations of petroleum in soils and upon human health, the specific fuel nondefault closure levels have maximum limits applied. It is generally recognized that the toxicity, (human and environmental), of petroleum products increases as the molecular weights of the compounds decrease. Research has demonstrated that lighter oils have demonstrated phytotoxic effects at concentrations as low as 1,000– 1,200 mg/kg. As a result, maximum soil TPH closure levels (caps) are set at different levels for gasoline and diesel, both residential and commercial/industrial, but in neither case may the soil attenuation capacity (SAC) be exceeded or free product exist. These limits apply even when a nondefault site specific soil attenuation capacity (SAC) exceeds them.

8.3.4 Exposure Prevention Remedies

Sites using exposure prevention remedies (those remedies that eliminate an exposure pathway by using institutional and/or engineering controls) can have soil concentrations exceeding Non-default maximum caps, but cannot have free product. Ground water TPH closure levels are not capped, but no free product may exist. COC closure levels must be met in both the soil and ground water.

8.3.5 Chemicals of Concern (COCs)

Petroleum releases are still required to meet the closure levels for the applicable COCs. Chemicals of concern for each of the hydrocarbon product types are discussed further in the RISC User's Guide, Chapter 3, Leaking Underground Storage Tanks, and Appendix 4.1. The analytical procedures for the COCs are described in Appendix 2 of the RISC Technical Guide.

8.4 Site Characterization

8.4.1 Characterizing TPH in Soil

Sites are normally evaluated in a step-wise procedure that involves screening the area to determine what areas contain contaminants of concern, and then determining the nature and extent of the contamination. Once the nature and extent of contamination is known, then a potential exposure concentration (PEC) can be determined and compared to the default or nondefault closure levels to see if a site is eligible for closure or requires remediation.

At petroleum release sites where the source, location, and type of material are known, such as at a leaking underground storage tank (LUST), screening and determining the nature and extent of contamination can be combined into an expedited process. Chapter 3 and Appendix 4.2 of the RISC User's Guide provide more information on evaluating LUST sites.

8.4.1.1 Screening

Sites with leaking underground storage tanks should follow the special procedures outlined in Appendix 4.2 of the RISC User's Guide. Sites that do not involve leaking storage tanks should apply the recommendations of the RISC Technical Guide, Chapter 3.

8.4.1.2 Nature and Extent of Contamination

Sites with leaking underground storage tanks should follow the special procedures outlined in Appendix 4.2 of the RISC User's Guide. Sites that do not involve leaking storage tanks should apply the recommendations of the RISC Technical Guide, Section 4.4.1. Consistent with RISC, the nature and extent of TPH and COC contamination should be delineated out to the residential closure level at all sites. The nature and extent of the TPH contamination should first be determined by using the appropriate (SW-846-8015D) GRO analysis for gasoline range products and ERO analysis for diesel and other mid-range and high end hydrocarbon oils. These concentrations will be used for calculating the potential exposure concentration (PEC). If it is anticipated that a nondefault closure level will be sought, then samples for fractionation analysis of the most heavily TPH contaminated soil should be taken first (See Section 5.0). The resultant nondefault residential closure level should then be used to define the nature and extent of contamination using the SW-846-8015D method.

8.4.1.3 Determining the PEC

The PEC can be calculated in different ways, depending upon the site specific situation. For sites not regulated by the LUST program, determine the PEC according to Chapter 3, Area Screening, of the RISC Technical Guide. For sites regulated by the LUST program, determine the PEC according to Appendix 4.2 of the RISC User's Guide.

8.4.2 Characterizing TPH in Ground Water

Ground water screening for TPH should be conducted in accordance with the default guidance presented in Section 3.4.5 of the RISC Technical Guide. Ground water contaminant plumes should be screened out to the residential closure level. Determine the nature and extent of TPH in the ground water according to the recommendations of Section 4.4.2 of the RISC Technical Guide.

8.5 Determining Closure

A stepwise approach is recommended for TPH sites. The nature and extent of the contamination should first be determined by using the appropriate (SW-846-8015D) GRO analysis for gasoline and ERO analysis for diesel and other mid range and high end hydrocarbon oils. Determine the PEC from the GRO/ERO analyses. If the PEC is below

the applicable default closure level, then the site is eligible for closure for TPH. If the PEC exceeds the applicable default closure level, the site should either be remediated or further evaluated by fractionating samples of the petroleum product to determine a site specific nondefault closure level.

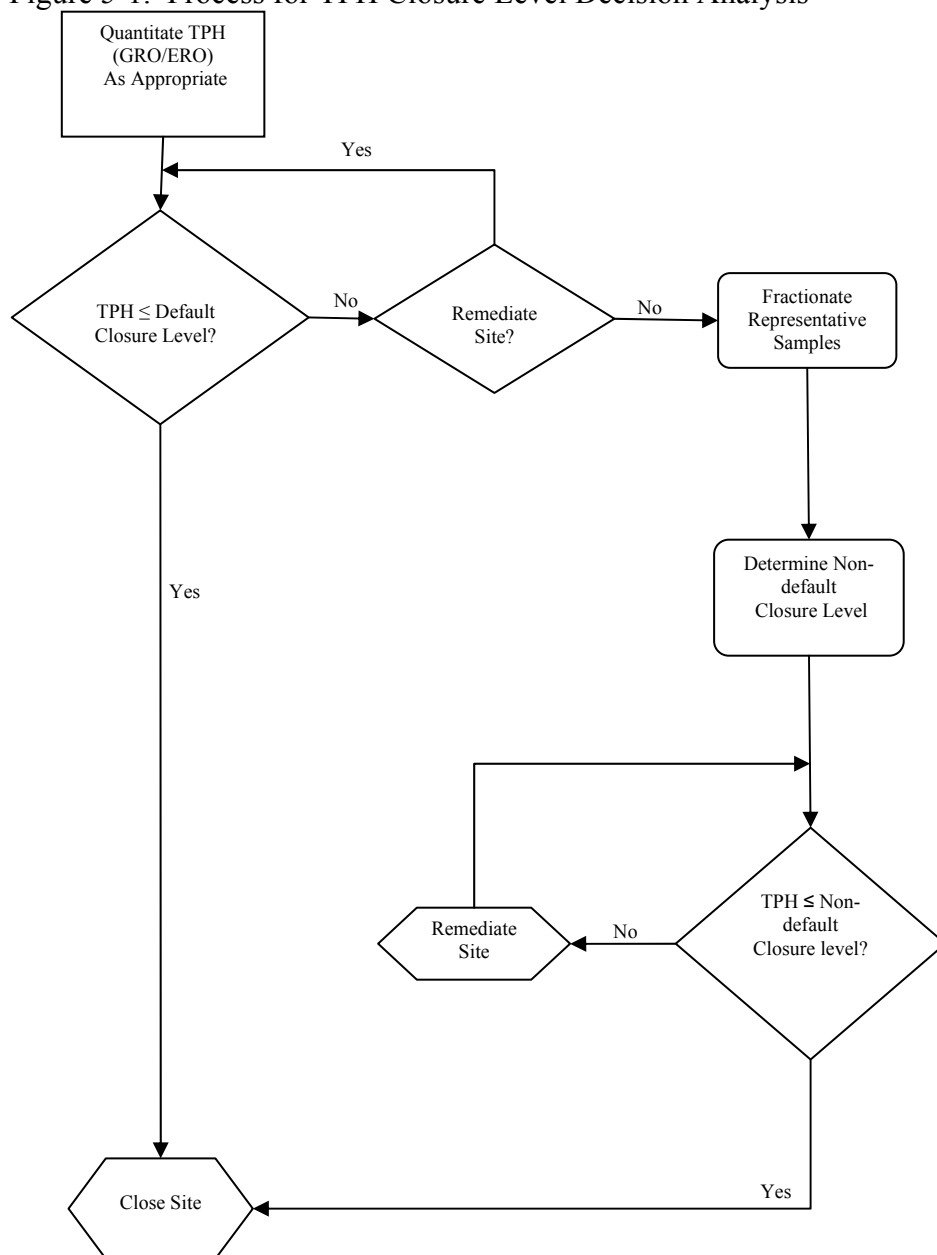
To determine nondefault soil and ground water TPH closure levels, three to five samples of the most heavily contaminated soil should be analyzed using the fractionation method (Section 7.2.2). The lowest (most conservative) closure level should be selected as the nondefault for the site. To avoid double counting the EC>8 – 10 and EC>10 - 12 fractions, use the higher of the VPH or EPH analysis to represent these fractions.

Determine the nondefault site-specific TPH soil closure level from the RISC TPH Spreadsheet (*to be posted on the IDEM web at: <http://www.in.gov/idem/programs/land/risc/index.html>*) and compare it to the non-default closure level cap. If the site-specific closure level is below the closure level cap, then the site-specific closure level is applied to the entire site. If the site-specific closure level exceeds the closure level cap, then the cap is applied to the entire site. Once site-specific TPH closure levels have been determined using fractionation analysis, compliance with nondefault site-specific closure levels can be demonstrated using simple TPH GRO or ERO (SW-846-8015D) analyses. If the fractionation analysis shows that the contaminant is a mixture of gasoline and diesel fuel, then use the sum of GRO + ERO. Figure 5-1 illustrates the process. As a general rule, mixtures of gasoline and diesel fuel should be compared to the gasoline closure level cap.

As specified in the RISC Technical Guide, Section 6.3.3.1, ground water closure levels must be met throughout the ground water plume for 8 consecutive quarters.

Consistent with RISC, contamination in excess of the residential closure level requires that controls are in place to assure that the public is not exposed to excess risk. See Chapter 6, Closure, of the RISC Technical Guide.

Figure 5-1. Process for TPH Closure Level Decision Analysis



8.6 Sample Collection

Proper sample collection and preservation is critical to obtaining accurate measurements of TPH in the environment. TPH samples, especially unknown petroleum products and gasoline range organics (GRO) samples, should be collected and preserved in a manner that minimizes the volatilization and biodegradation of the hydrocarbons. Studies of samples with low concentrations of VOCs (less than 200 ppb) in soils have shown losses of 80% - 95% when using the traditional soil collection procedure of putting the soil into four ounce jars. Because of this, TPH soil samples for gasoline and unknown petroleum products should be taken in accordance with EPA's Method SW-846-5035A, Appendix A, or Indiana's method IN-5035M, found on IDEM's web site at:

<http://www.in.gov/idem/programs/land/hazwaste/guidance/inmodifiedmethod5035.pdf>

If it is anticipated that a site-specific TPH closure level will be determined by fractionation, collect duplicate TPH samples so that when the appropriate samples are identified by the standard analytical method (SW-846-8015D) GRO or ERO analysis (extended range organics, C₈ – C₃₆), sufficient samples are available for fractionation (provided analytical holding times can be met). Sampling the ground water for TPH is not affected (see Table 7-1).

It should be pointed out that, while in the past the mid-range hydrocarbon products (*e.g.* diesel) have been characterized by the diesel range organics (DRO, C₈-C₂₈), IDEM is now requiring that the extended range organics (C₈-C₃₆) be used. This will facilitate the comparison of the ERO analyses with the fractionation derived closure levels.

8.7 Sample Analysis

8.7.1 TPH Classes

For the purposes of TPH laboratory analysis in this guidance, petroleum products are broken down into four general classes of TPH:

- Gasoline Range Organics (C₅ – C₁₂)
- Mid-Range Liquid Hydrocarbon Products or Diesel Range and Extended Range Organics (C₈ – C₃₆)
- High End Hydrocarbon Oils (C₈ – C₃₆)
- Waste Motor Oil (C₈ – C₃₆)

See Table 7.1 for further explanation of the classes and recommended TPH and COC analytical methods.

8.7.2 TPH Analytical Methods

Because the standard DRO analysis for diesel often stops at C₂₈ compounds, and the fractionation analysis goes to C₃₆ compounds, it is recommended that diesel fuel and other mid-range hydrocarbon product contamination be characterized by running the extended range organics analysis (to C₃₆) to facilitate comparison with the fractionation analysis derived closure levels. Table 7.1 presents the various petroleum products and COCs and their appropriate analytical methods for default closure levels.

8.7.2.1 Determining Nature and Extent of Contamination and Potential Exposure Concentrations

The analytical method for determining the nature and extent of contamination and the potential exposure concentration (PEC) is SW-846-8015D. For gasoline contamination, use the GRO analytical range. For diesel and other mid-range petroleum products, use the ERO analytical range. If there is any possibility of a mixture of gasoline and diesel, then both the GRO and ERO analytical ranges should be run and compared to the default mixed contaminant closure level as determined in Section 3.1.

8.7.2.2 Determining Site Specific (Non-default) Closure Levels

Non-default uses fractionation of the TPH sample for determining site and product specific closure levels. The analytical methods to be followed are the Washington Department of Ecology's VPH/EPH methods. These methods can be found at <http://www.ecy.wa.gov/biblio/97602.html>. A Level 4 Data Quality Package should be submitted with the analytical results.

Table 7.1 Recommended Sample Collection and Analytical Methods

Product	TPH		COC		
	Sample Collection and Preparation	Analytical Method	COCs	Sample Collection	Analytical Method
Gasoline Range (C ₅ - C ₁₂) Auto gasoline Aviation gas Racing gas Mineral spirits Stoddard solvents Naptha Jet fuel JP-4	5035A/IN5035M (Soil) 5030B (Water)	SW-846-8015D	BTEX MTBE n-Hexane Naphthalene	5035A/IN5035M (Soil) 5030B (Water)	GC/PID 8021 or GC/MS 8260 or GC/MS 524.2
Diesel Range (C ₈ - C ₃₆) No 1 Diesel No 2 Diesel Kerosene Jet fuel (J-5, -7, -8) Light oil Home heating oil	Traditional with Appropriate Extraction	SW-846-8015D	cPAHs Naphthalene BTEX MTBE	5035A/IN5035M (Soil) 5030B (water) and Traditional with Appropriate Extraction	GC/PID 8021 or GC/MS 8260 or GC/MS 524.2 and GC/MS 8270 SIM or HPLC 8310 or GC/MS 525.2
High End Hydrocarbon Oils (C ₈ - C ₃₆) No 4 Fuel oil No 5 Fuel oil No 6 Fuel oil Bunker C Mineral oil	Traditional with Appropriate Extraction	SW-846-8015D	PAHs and Naphthalene	Traditional with Appropriate Extraction	GC/MS 8270 SIM or HPLC 8310 or GC/MS 525.2
Waste Oil*	Traditional with Appropriate Extraction	SW-846-8015D	VOCs PAHs PCBs Metals*	Traditional with Appropriate Extraction	GC/PID 8021 or GC/MS 8260 or GC/MS 524.2 8310 or 8270 SIM or 525.2 and Relevant SW 846 methods for metals 8082

* See *Waste Oil Analyses and Analytes*, at
http://www.in.gov/idem/programs/land/lust/waste_oil.html